1962

Reaction of hydrogen with solutes in metals

Ralph Wendell Curtis
Iowa State University

REACTION OF HYDROGEN WITH SOLUTES IN METALS

by

Ralph Wendell Curtis

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1962

TABLE OF CONTENTS

I. INTRODUCTION

The reaction of hydrogen with metals has been a subject of interest for a number of years. However, in recent years a great deal of emphasis has been placed on the reaction of hydrogen with alloys. The reaction of hydrogen with solutes in metals as a method of separating solute impurities as hydrides from liquid metal solutions by hydrogen/liquid metal reactions was investigated by Woerner (1). The investigation conducted by Woerner consisted of measuring the amount of solute metal removed from a liquid solution at one atmosphere hydrogen pressure and at various temperatures. He found that the concentrations of the solutes in liquid solutions were reduced by one atmosphere hydrogen pressure for the following systems: calcium, cerium, lanthanum, yttrium, and thorium as solutes in magnesium; thorium as the solute in magnesium-55 wt. % zinc; and thorium as the solute in magnesium-30 wt. % aluminum. He also found that hydrogen had no effect on reducing the concentration of yttrium or thorium in liquid zinc nor on the concentration of zirconium in liquid aluminum.

Denver Research Institute (2) made an extensive study of the hydriding characteristics of various binary intermetallic compounds. They classified the compounds into one of three groups on the basis of the products formed on hydriding. They consider the first group to be hydride

formers or those binary intermetallic compounds which actually form a ternary compound with hydrogen. An example of this type is Zr_2Al which forms Zr_2AlH_x ($x = 2.7$). The second group includes those compounds which are inert to hydrogen at elevated temperatures and the third group consists of those compounds which react with hydrogen to form two or more different compounds. An example of the second and third types of intermetallic compounds are $ZrAl_2$ and Zr_3Al respectively. When Zr_3Al was reacted with hydrogen the resulting compounds were found to be ZrH_2 and Zr_2AlH_3. The researchers point out that if the intermetallic compound fell into the third group, the products, in many cases, were extremely difficult to identify. In their study they found 8 intermetallic compounds which could be classified as intrinsic hydride formers. They found 55 compounds which were inert to hydrogen and 37 which absorbed large amounts of hydrogen and broke down into at least two distinct phases.

The primary purpose of this research was to investigate the applicability of the reaction of hydrogen with solutes in binary metal solutions as a method for determining the thermodynamic properties of intermediate phases existing between the two metals. Equilibrium hydrogen pressures can usually be readily measured with good precision. Such a method would have a number of advantages and hopefully can be applied to systems which are not readily investigated by

other methods. The metals which form stable hydrides of fairly well defined stoichiometry are the alkali, alkaline earth and rare earth metals and some of the Group III A and Group IV A transition metals. The first group of metals is very reactive and the thermodynamic properties of their alloys can not be readily measured by the usual e.m.f. or dew-point method. The transition metals usually have too low a vapor pressure to be studied by the Knudsen or dew-point method except at very high temperatures. Consideration of the available free energy data for the hydrides and the free energy of formation of intermetallic phases suggests that it may be possible to establish, in favorable cases, an equilibrium of the type

$$AB_2(s) + H_2(g) \rightleftharpoons AH_2 + B(s).$$

As implied by this reaction one of the components, A, forms a stable hydride whereas B does not. An example of such an alloy is the compound $CaMg_2$. Consequently, knowledge of the thermodynamic properties of the hydride along with the measured equilibrium hydrogen pressures would permit calculation of the thermodynamic properties for the compound AB_2. The primary disadvantage of this method arises from the fact that a third component, hydrogen, is involved. As was already indicated above, ternary hydrides might be formed and the actual equilibrium phases may be very complex. In any case it is necessary to carefully identify the equilibrium

phases formed.

In the case of the calcium-magnesium system the equilibrium reaction can be written as

$$CaMg_2(s) + H_2(g) \rightleftharpoons CaH_2(s) + 2Mg \text{ (Mg-rich solid solution)}.$$

At equilibrium four phases exist and from the Gibb Phase Rule it may be shown that only one degree of freedom remains. Consequently, at any given temperature the compositions of the phases and the hydrogen pressure are fixed. The free energy change for the reaction at equilibrium can be written as

$$\Delta F = \Delta F^{\circ}_{CaH_2} - \Delta F^{\circ}_{CaMg_2} - RT \ln P_{H_2} + 2\overline{\Delta F}_{Mg} = 0$$

where $\overline{\Delta F}_{Mg}$ is the partial molar free energy of solution of magnesium in the liquid or solid solution present at equilibrium. If the standard free energy of formation for the hydride and the partial molar free energy of solution for magnesium are known, along with the measured equilibrium hydrogen pressure over the system as a function of temperature, it is possible to calculate the thermodynamic quantities for the formation of $CaMg_2$. In this case the solution formed is composed primarily of magnesium and one can assume that the activity of magnesium in this solution is approximately unity.

The calcium-magnesium system was the system of primary interest in this investigation. The thermodynamic properties

of calcium hydride are essential in this case. Since there was some doubt concerning the validity of available thermodynamic data for this compound the dissociation pressure was reinvestigated.

Previous work on the calcium hydrogen system includes the measurement of equilibrium hydrogen pressures over the system consisting of calcium and calcium hydride by Treadwell and Stecher (3) and Johnson et al. (4). The results of their investigations were expressed as

$$\log P_{H_2}(\text{atm}) = \frac{-9840}{T} + 7.32$$

and

$$\log P_{H_2}(\text{atm}) = \frac{-10,820}{T} + 8.612$$

respectively, for the temperature range 778-900°C. Brönsted (5) measured the dissociation pressure of calcium hydride in the temperature range 641-747°C. He obtained from his data a value of -43,900 cal/mole for the room temperature heat of formation for calcium hydride. Brönsted also determined the heat of formation from calorimetric measurements on the heat of solution of calcium and the hydride. These measurements gave a room temperature value of -45,100 cal/mole. Lewis and Randall (6), after reevaluating the difference in heat capacity of the products and reactants for the calcium hydride decomposition, derived an expression for the free energy which was consistent with Brönsted's (5) dissociation pressures and room temperature calorimetric enthalpy. Lewis

and Randall point out, however, that the calculated entropy change for the dissociation, 34.6 cal/mole ^{o}C, is probably about 4 entropy units too large.

A study of the allotropic modifications of calcium and the effect of various impurities on the transformations has been carried out by Smith and Bernstein (7) and by Smith, Carlson and Vest (8). The phase diagram for the calcium-calcium hydride system has been determined by Peterson and Fattore (9). These new data and the availability of high purity calcium prompted a reinvestigation of the dissociation pressure of calcium hydride.

Previous work on the calcium magnesium system includes the determination of the thermodynamic properties of $CaMg_2$ by Smith and Smythe (10). Their results, based on vapor pressures obtained by a Knudsen effusion cell, can be represented by

$$\Delta F^{o}_{CaMg_2} = -8,400 + 1.2T \text{ in cal/mole.}$$

Smith (11) reports a value of -6,900 cal/mole for the enthalpy of formation of $CaMg_2$ as determined by combustion calorimetry and a value of -13,000 cal/mole as calculated on the basis of crystal structure data by Kubaschewski's method (12). Much higher values for the heat of formation of $CaMg_2$ are tabulated by Rossini et al. (13) and Kubaschewski and Evans (14) who give -30 and -21.3 K cal/mole respectively. Woerner (1) also determined the thermodynamic properties of

$CaMg_2$ using a method similar to that employed in this investigation. His results for the free energy of formation of $CaMg_2$ can be expressed as

$$\Delta F^{o}_{CaMg_2} = -28,378 + 24.042T.$$

The phase diagram for the calcium-magnesium system as reported by Hansen and Anderko (15) is reproduced in Figure 11.

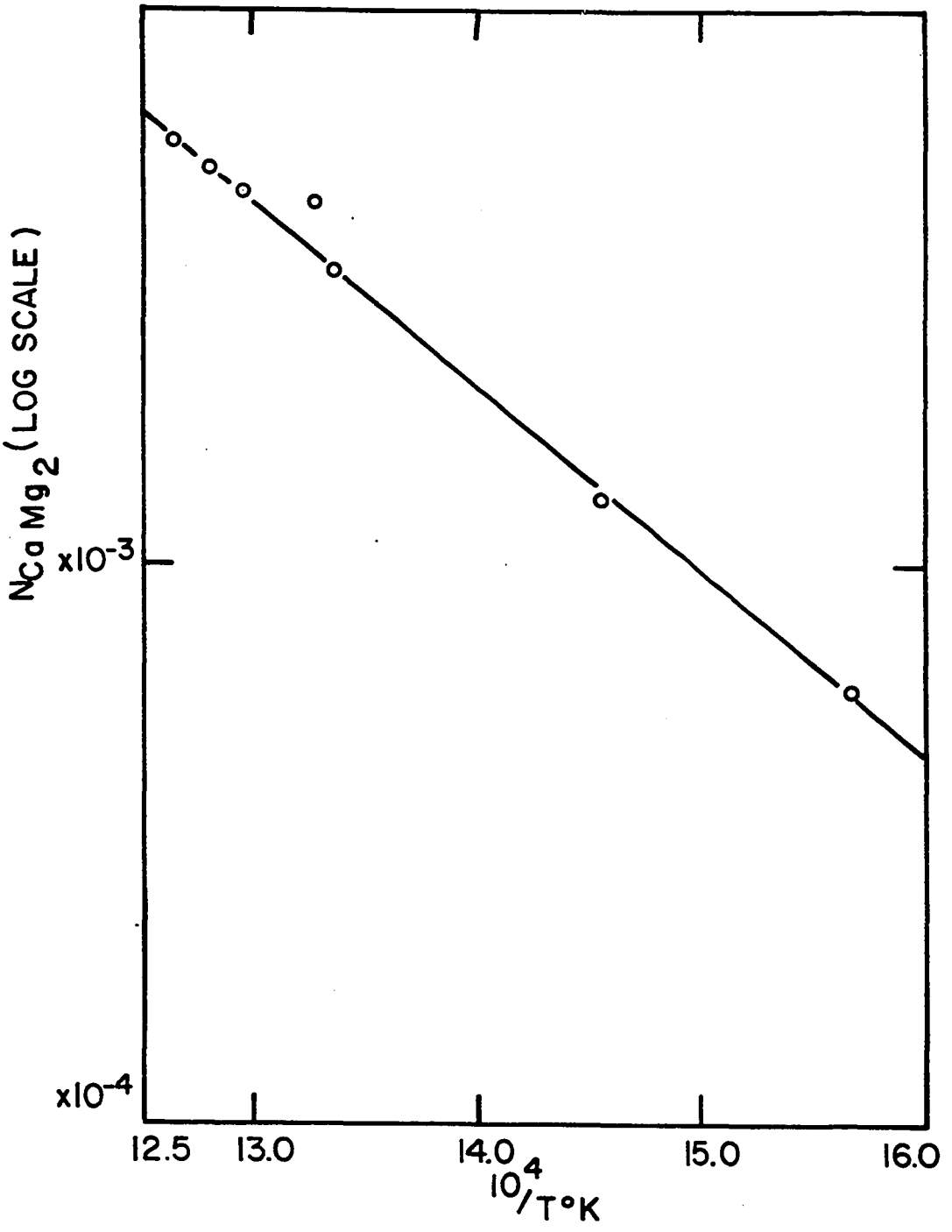
The solid solubility of calcium in magnesium has been determined by Burke (16). His data are given in Table 1 and

Table 1. Solid solubility of calcium in magnesium according to Burke (16)

Temp.°C	$10^4/T^{o}K$	Weight % Ca	$N_{CaMg_2} \times 10^3$
365	15.67	0.10	.61
415	14.54	0.22	1.34
476	13.35	0.56	3.43
481	13.26	0.74	4.54
499	12.95	0.78	4.78
508	12.80	0.86	5.29
518	12.64	0.95	5.85

plotted as log $N(CaMg_2)$ vs $10^4/T^{o}K$ in Figure 1. If one assumes that the activity of magnesium in the magnesium rich solution is unity, it can be shown that $\Delta H^{o}_{CaMg_2} = -\overline{\Delta H}_{CaMg_2} + \overline{\Delta H}_{Ca}$. Since the solid solution and the

Figure 1. Mole fraction $CaMg_2$ in the magnesium-rich calcium-magnesium solid solution as a function of temperature


$N_{Ca\,Mg_2}$ (LOG SCALE)
x10^{-3}
x10^{-4}
12.5
13.0
14.0
15.0
16.0
10^4/T°K

compound are in equilibrium, the activity of $CaMg_2$ in the solution is unity. If one considers Henry's law to hold for the magnesium-rich solution it can be shown, (17) (See Appendix), that

$$\left(\frac{\partial \ln N(CaMg_2)}{\partial 1/T}\right)_p = \frac{-\overline{\Delta H}_{CaMg_2}}{R}.$$

Therefore,

$$-\overline{\Delta H}_{CaMg_2} = \left(\frac{2.3R\partial \log N_{CaMg_2}}{\partial 1/T}\right)_p = -15{,}000,$$

as evaluated from the slope of the line in Figure 1. Then

$$\Delta H^{o}_{CaMg_2} = -15{,}000 + \overline{\Delta H}_{Ca}.$$

If $\overline{\Delta H}_{Ca}$ could be determined this would provide another method for determining the standard enthalpy of formation of $CaMg_2$.

An attempt was also made to measure the equilibrium hydrogen pressure over various other binary systems in an effort to evaluate the utility of this method for determining thermodynamic properties of intermediate phases. A brief exploratory investigation was made for the following systems: calcium-lead, calcium-silver, thorium-silver, and thorium-copper.

II. THERMODYNAMIC PROPERTIES OF CaH_2

Materials and Apparatus

The calcium employed in this study was purified at Ames Laboratory (8). The analysis of the metal is given in Table 2. High purity hydrogen was obtained by the decomposition of UH_3.

Table 2. Chemical analysis of Ames Laboratory purified calcium

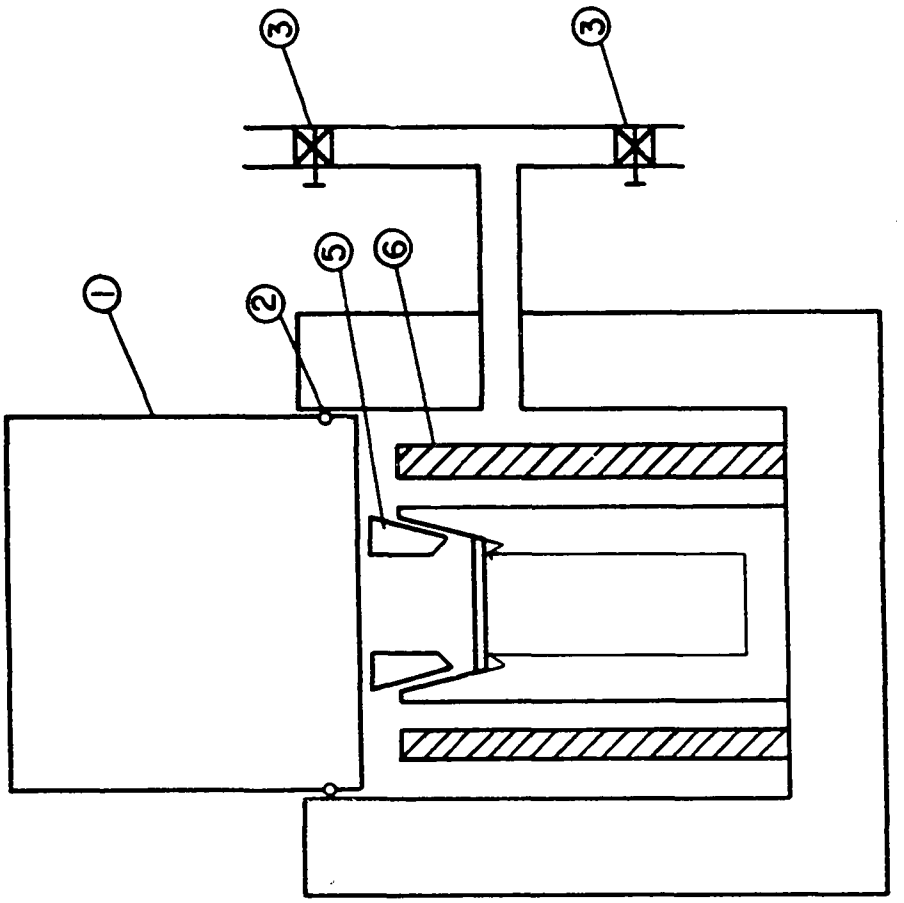
Element	Content (ppm)
Mg	250
C	200
O	~100
N	50
Fe	5
Others	<1

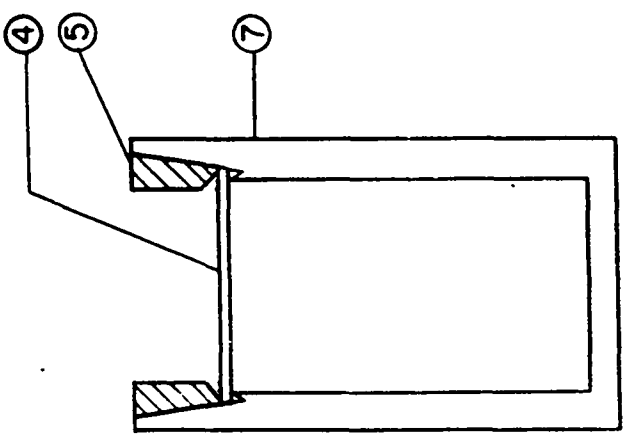
The crucible material used to contain the calcium-calcium hydride mixture consisted of commercial Armco iron containing 165 ppm carbon. A one mil steel sheet which was used to seal the crucible to prevent vaporization of the calcium was decarburized. This was done by sealing the thin sheet inside a one inch tantalum crucible containing metallic calcium. The crucible and its contents were then placed in

an oscillating furnace and heated to 875°C. The furnace was then rocked through an arc of approximately 120° once every 5 seconds for 2 hours to ensure good contact between the molten calcium and the steel sheet. The carbon content was reduced from 1000 to 250 ppm by this treatment. Low carbon iron was employed to avoid contamination of the calcium with carbon and as a precaution against the possible formation of methane. The reaction $Fe_3C + 2H_2 \longrightarrow 3Fe + CH_4$ is thermodynamically favorable in the lower temperature range of the present investigation and could introduce an appreciable error in the measured equilibrium hydrogen pressure. The rate of hydrogen diffusion through the thin steel sheet was also increased by the lower carbon content. The apparatus used was similar to the apparatus employed by Woerner (1). In order to study the dissociation pressure of the hydride it was necessary to seal the sample inside an iron crucible fitted with a thin iron diaphram. The diaphram, made from one mil iron sheet, is impervious to calcium vapor but pervious to hydrogen. A similarly sealed crucible was employed by Johnson et al. (4). They point out that the reaction of calcium vapor with quartz caused erroneous results in the measured hydrogen pressure. Figure 2 shows a schematic diagram of the iron crucible used to contain the sample and the apparatus used to seal the crucible assembly under an atmosphere of hydrogen. The crucibles, 2" long by

Figure 2. Schematic diagram of crucible and die assembly used to seal the crucible

1. Steel plunger
2. "O" ring to form vacuum seal
3. Pinch clamps
4. One mil iron foil used as a semi-permeable membrane
5. Cylindrical cap used to form seal
6. Steel cylinder to stop plunger
7. Armco iron crucible


3
3
5
6
1
2

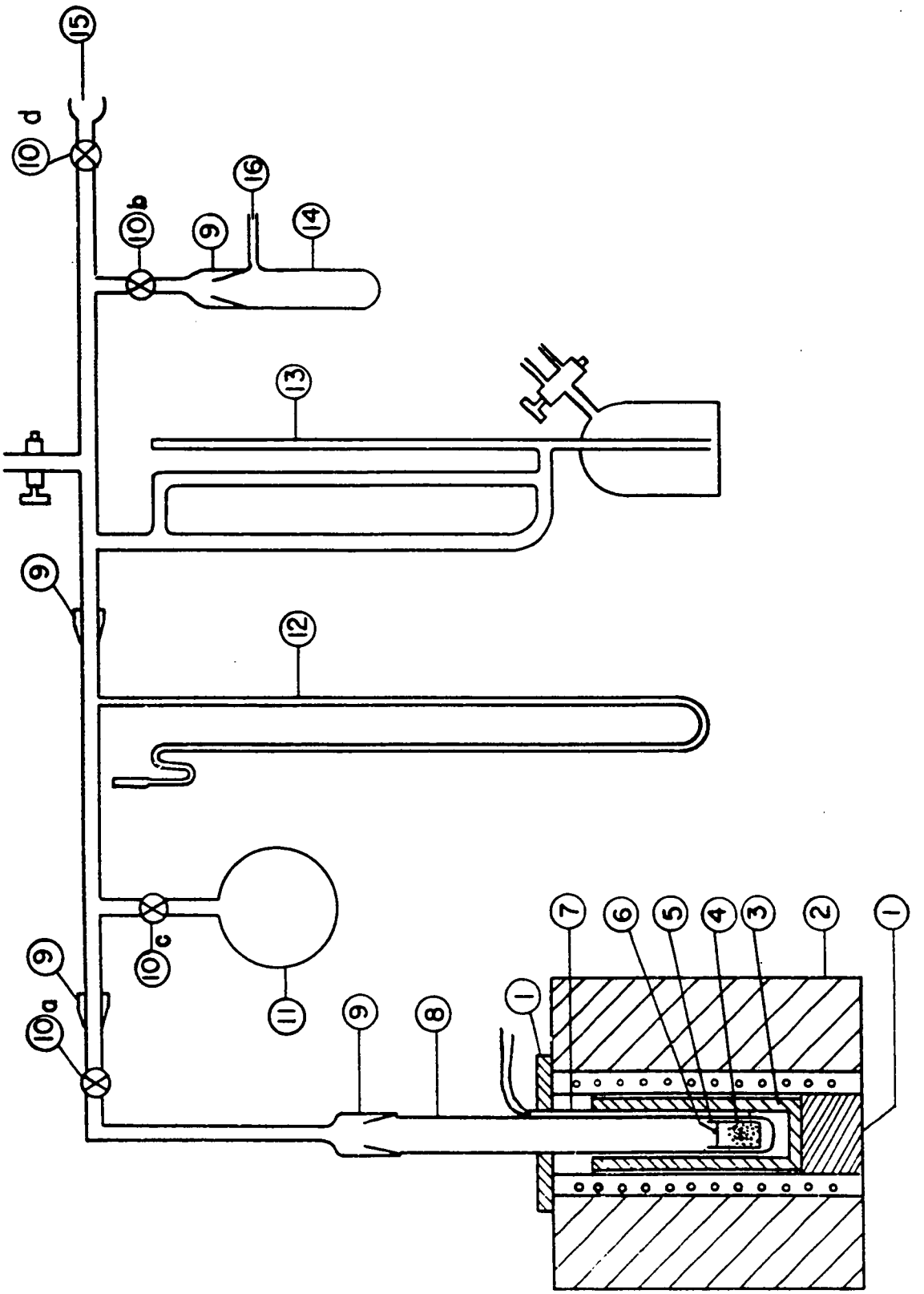

4
5
7

1/2" inside diameter, were made from 3/4" Armco iron rod. The inside diameter at the top of the crucible was machined to a depth of 3/8" forming a small shoulder around the inside of the crucible. This shoulder was machined so that it tapered to the outside. The purpose of the shoulder was to provide a means of supporting the thin steel diaphram. The thin circular sheet of iron was held in place by a tapered cylinder of Armco iron with an outside taper of 6 mil per inch which was equal to the taper cut in the top of the iron crucible. A gas tight seal was formed between the iron foil diaphram and the shoulder on the inside of the crucible by forcing the tapered cylinder into the top of the crucible with a hydraulic press. The steel sealing device used to cap the iron crucible shown in Figure 2 consists of a solid metal plunger which fits into a die. An "O" ring seal was used between the plunger and die to form a vacuum seal. The die was evacuated and filled with gas by means of a metal tube connected to the side. A metal cylinder was provided inside the die to prevent the plunger going too far and consequently deforming the crucible.

A schematic diagram of the system used in the measurement of equilibrium hydrogen pressures is shown in Figure 3. Two such apparatuses were used in the measurements but since they vary only in volume and McLeod gauge sensitivity only one will be described to simplify the discussion. The

Figure 3. Schematic diagram of the system used to measure the equilibrium hydrogen pressures

1. Fire brick insulation
2. Split-type resistance furnace
3. Stainless steel liner
4. Metal sample
5. Armco iron crucible
6. One mil iron foil
7. Alumel-chromel thermocouple
8. Quartz reaction tube
9. Ground glass joints
10. Stopcocks
11. One liter flask
12. Manometer
13. McLeod gauge
14. Quartz tube containing UH_3
15. To vacuum system
16. Hydrogen inlet


15
10d
16
10b
9
14
13
6
12
10c
11
9
10a
8
1
7
6
5
4
3
2
1

apparatus was constructed of pyrex with the exception of the reaction tube, 8, and the tube containing uranium hydride, 14, which were both made of 21 mm inside diameter quartz tubing. These were connected to the system by means of tapered, ground glass joints. The joints were sealed with Apiezon wax in order to maintain a high vacuum. The reaction tube extended into the furnace about 12 inches. A stainless steel cylinder about 6 inches long with 1/8 inch walls and a 1/4 inch bottom was situated around the bottom of the reaction tube in order to provide a constant temperature zone. This arrangement provided a constant temperature zone of about 3 inches. A small slot was machined on the inside of the stainless steel liner to provide a method of holding the thermocouple in place. The stopcocks used in the apparatus were 4 mm, high vacuum, hollow plug, oblique bore stopcocks. Extra volume was provided by a flask having a volume of approximately one liter. The volume of the flask was accurately determined prior to the assembly of the system in order to provide a method for determining the volume of the rest of the system. The system was calibrated by admitting a given amount of hydrogen to the system with stopcock 10c open. The pressure was recorded, stopcock 10c was closed and the system was evacuated. Stopcock 10d was closed, stopcock 10c was opened and the pressure was again recorded. The volume of the system was determined from the

expression $P_1V_1 = P_2V_2$. A correction was made for the volume of mercury displaced in the manometer, the results were averaged and the volume of the system, including the calibrated reservoir, was calculated to be 1.576 liters. Pressures of 2 cm of mercury or greater were measured by means of the closed end manometer while those of lower magnitude were measured by means of the McLeod gauge. The gauge reading R in centimeters was related to the pressure in atmospheres by the relation

$$P(atm) = 3.4245 \times 10^{-6}R^2.$$

A McLeod gauge reading of one centimeter was the lowest pressure considered. At this pressure the leak rate of the system was negligible. No change in the McLeod gauge reading could be detected after periods as long as three days.

The vacuum system used in conjunction with the apparatus described above consisted of a mechanical pump, a mercury diffusion pump and a liquid nitrogen cold trap. A vacuum of 3×10^{-6} mm of mercury was obtainable with this system. The sample was heated by means of a one inch diameter split type resistance furnace. The power was supplied by a 220 volt constant voltage source. The temperature was controlled by means of a Leeds and Northrup, Speedomax Type H, indicating and recording controller used in conjunction with a Leeds and Northrup, Series 60, single action control unit and a Barber-Colman reversible motor. The temperature was

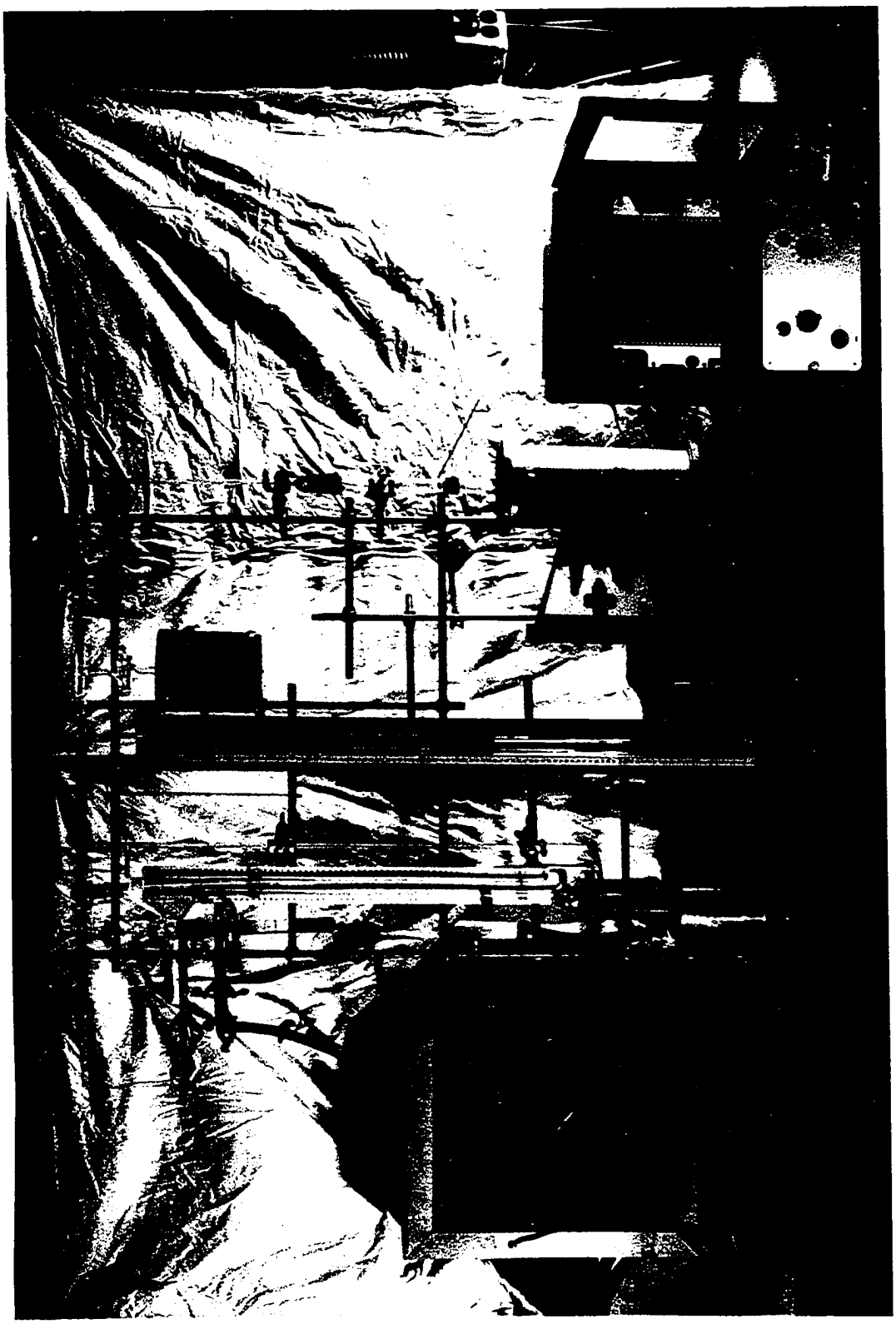
controlled to within $\pm$ 1/2°C with this system. The temperature of the sample was measured with a Rubicon potentiometer. A photograph of the hydrogen equilibration apparatus and temperature controller is shown in Figure 4.

Experimental Procedure

An Armco iron crucible assembly was outgassed at 900°C for 12 hours under a vacuum of 1×10^{-5} mm Hg. The crucible assembly was removed from the apparatus and a sample of calcium weighing approximately two grams was sealed inside the crucible under a hydrogen atmosphere. The crucible was sealed by means of the sealing apparatus described above as follows: The iron crucible, cap and iron foil were positioned in the steel die and the plunger was inserted. The system was evacuated by opening the pinch clamp leading to a vacuum pump. The die was filled with hydrogen and evacuated several times then sealed off under approximately one atmosphere of hydrogen pressure by closing both pinch clamps. The die was placed in a hydraulic press and the plunger was forced down, thus forcing the tapered cylinder down onto the shoulder of the crucible forming a gas tight seal against the iron foil diaphram.

The crucible and its contents were placed in the reaction chamber shown in Figure 3 and the reaction tube was sealed in place with Apiezon wax. The apparatus was evacu-

Figure 4. Photograph of the system used in measurement of the equilibrium hydrogen pressures



ated and stopcock 10b was opened, stopcock 10d was closed and the uranium hydride was heated until a given amount of hydrogen had been introduced into the system. The amount of hydrogen admitted was just enough to convert about half of the calcium to calcium hydride. After the hydrogen was added stopcock 10b was closed and the reaction tube was heated to approximately 700°C to permit the hydrogen to diffuse through the one mil iron diaphram and react with the calcium. After the pressure attained a constant value the system was evacuated. In all cases the pressure returned to the same equilibrium value. The amount of hydrogen removed during the time the system was evacuated was small compared to the total amount of hydrogen originally admitted to the system. The time to attain equilibrium varied from 16 hours at 888°C to 2 days at 596°C. After the pressure remained constant for a period of 8 to 12 hours the system was assumed to be at equilibrium. It was found that the equilibrium pressures were not dependent on whether the equilibrium was approached from higher or lower pressures.

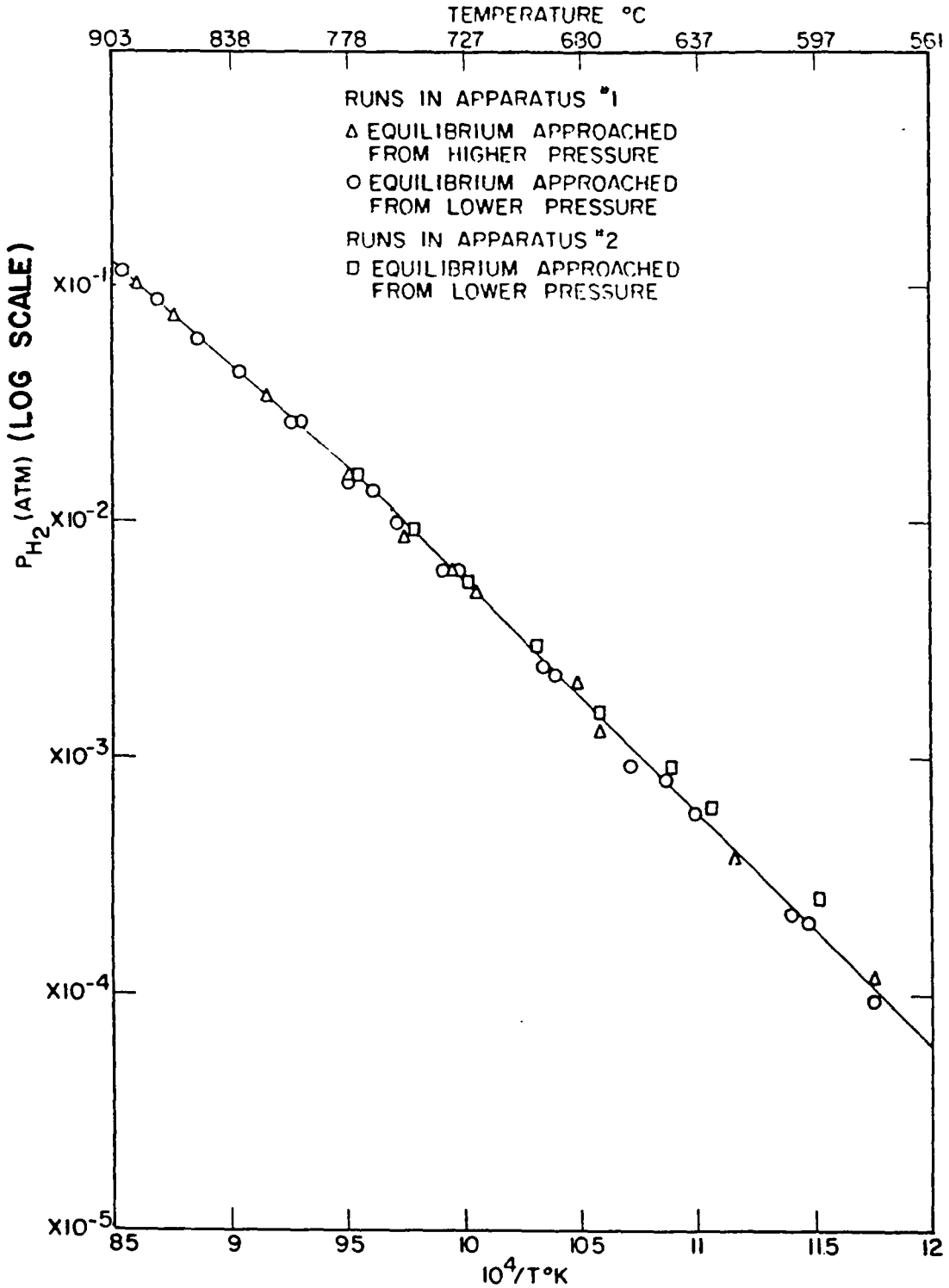
Experimental Results

The data obtained in this investigation are given in Table 3. The measured equilibrium hydrogen pressures are plotted as log P_{H_2}(atm) vs $10^4/T^\circ K$ in Figure 5. It is apparent from the data that a change in slope exists at

Table 3. Equilibrium hydrogen pressures measured over the calcium-calcium hydride system

Hydrogen pressure in atmospheres x 10^3	Temperature ^oK	$10^4/T^oK$
.1080	851	11.75
.2556	869	11.51
.2031	872	11.47
.2188	878	11.39
.3740	896	11.16
.6167	903	11.07
.5843	910	10.98
.9154	919	10.88
.8021	920	10.87
.9228	933	10.72
1.276	944	10.59
1.584	945	10.58
2.090	953	10.49
2.234	963	10.39
2.415	967	10.34
2.990	970	10.30
4.980	995	10.05
5.466	998	10.02
6.073	1003	9.97
6.243	1004	9.96
6.175	1009	9.91
9.242	1021	9.79
8.464	1026	9.75
9.916	1029	9.72
13.60	1041	9.61
15.79	1047	9.55
14.78	1051	9.51
15.60	1052	9.51
26.71	1074	9.31
26.79	1080	9.26
33.95	1092	9.16
43.55	1106	9.04
59.74	1127	8.87
74.34	1140	8.77
88.16	1151	8.69
100.3	1161	8.61
114.5	1171	8.54

Figure 5. Equilibrium hydrogen pressure measured over calcium-50 mole % CaH_2 as a function of temperature


TEMPERATURE °C
903
838
778
727
680
637
597
561
RUNS IN APPARATUS #1
Δ EQUILIBRIUM APPROACHED FROM HIGHER PRESSURE
O EQUILIBRIUM APPROACHED FROM LOWER PRESSURE
RUNS IN APPARATUS #2
□ EQUILIBRIUM APPROACHED FROM LOWER PRESSURE
P_{H_2} (ATM) (LOG SCALE)
X10⁻¹
X10⁻²
X10⁻³
X10⁻⁴
X10⁻⁵
85
9
95
10
105
11
11.5
12
10⁴/T°K

about 780°C. This is to be expected on the basis the solid state transformation as shown on the calcium-calcium hydride phase diagram, Figure 6. A least squares treatment of the data for the temperature range 578-780°C gives the following relation

$$\log P_{H_2}(atm) = \frac{-9610}{T} + 7.346. \qquad (1)$$

The standard deviations for the slope and intercept are 134 and 0.146 respectively. The data for the temperature range 780-900°C were fitted to the best straight line which intersects at 1053°K (780°C) the line represented by the above equation. The relation obtained can be represented by

$$\log P_{H_2}(atm) = \frac{-8890}{T} + 6.66 \ . \qquad (2)$$

The sealed crucible containing the calcium-calcium hydride sample was removed on completion of a run and placed in a dry box containing argon. The sample was finely ground in a porcelain mortar, screened through a 250 mesh screen, and placed in a 0.5 mm lithium glass capillary tube. Immediately after removal from the dry box the capillary was sealed with Apiezon wax and an x-ray diffraction pattern was taken with a Debye-Scherrer powder camera. The "d" spacings and relative intensities obtained from the sample were compared to those given in the A.S.T.M. Files (18). These data are tabulated in Table 4. The first 18 lines could be indexed on the basis of calcium hydride or calcium. Smith

Figure 6. Calcium-calcium hydride phase diagram (after Peterson and Fattore)

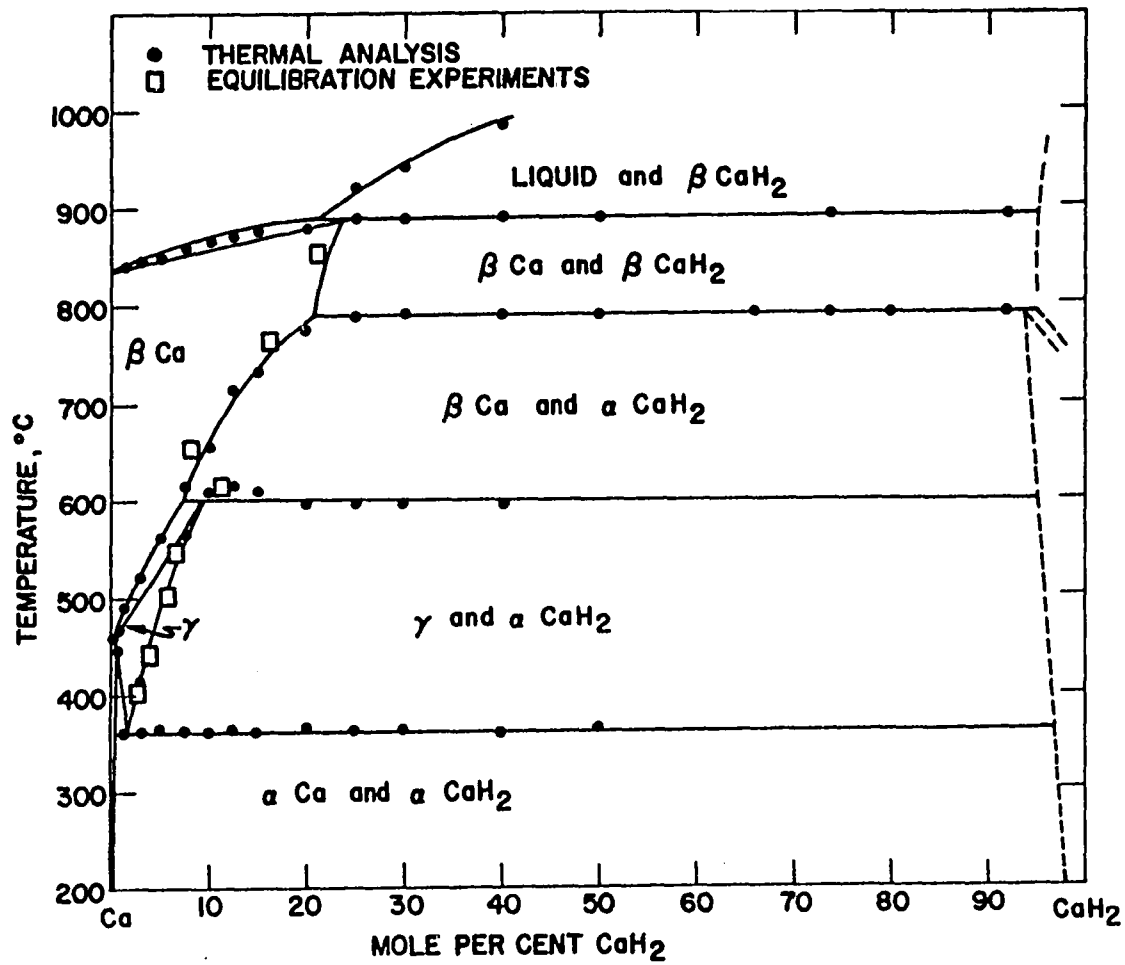

THERMAL ANALYSIS
EQUILIBRATION EXPERIMENTS
LIQUID and β CaH2
β Ca and β CaH2
β Ca
β Ca and α CaH2
γ
γ and α CaH2
α Ca and α CaH2
TEMPERATURE, °C
1000
900
800
700
600
500
400
300
200
Ca
10
20
30
40
50
60
70
80
90
CaH2
MOLE PER CENT CaH2

Table 4. Comparison of the observed "d" spacings and relative intensities obtained from the calcium-50 mole % calcium hydride samples to those given in the A.S.T.M. files for calcium and CaH_2

Observed relative intensity	Observed d	Literature values "d"-Ca	Ca Rel.Int.	"d"-CaH_2	CaH_2 Rel.Int.
S	3.17	3.21	100	3.18	40
VVS	2.96			2.97	100
VS	2.80	2.80	30	2.81	80
S	2.18			2.17	40
W	1.92	1.97	20	1.92	28
VW	1.83			1.82	8
VW	1.80			1.79	20
VW	1.72			1.71	24
VW	1.70				
S	1.68	1.68	20	1.68	24
S	1.61	1.61	10	1.61	20
S	1.54			1.54	36
VVW	1.49			1.48	8
VVW	1.48				
VVW	1.35			1.35	4
W	1.25	1.25	3	1.25	36
W	1.24				
VVW	1.18			1.18	8
VVW	1.16				
VVW	1.15	1.14	5	1.15	8
VVW	1.12			1.12	4
VVW	1.07			1.07	4
VVW	.955				
VVW	.953				
VVW	.949				
VVW	.947				
VVW	.872				
VVW	.866				
VVW	.863				
VVW	.823				
VVW	.822				
W	.798				
W	.796				
VVW	.775				

and Bernstein (7) point out that the structure of calcium is very sensitive to minor impurities. Therefore, the extra lines, all of which are extremely weak, may be due to minor impurities or to hydrogen dissolved in the metal. The work done by Peterson and Fattore (9), on the calcium-calcium hydride phase diagram, Figure 6, leaves little doubt that the phases present were calcium hydride and a solid solution of hydrogen in calcium.

Thermodynamic Analysis

The treatment of the data obtained can best be illustrated by the following equations:

$$\begin{aligned}
&Ca(\beta\text{-s}) + H_2(1\ atm) \longrightarrow CaH_2(s) && \Delta F = \Delta F^{o}_{CaH_2} \\
&Ca(\beta\text{-soln}) \longrightarrow Ca(\beta\text{-s}) && \Delta F = -\overline{\Delta F}_{Ca} \\
&CaH_2(s) \longrightarrow CaH_2(\alpha\text{-soln}) && \Delta F = \overline{\Delta F}_{CaH_2} \\
&H_2(P\text{-eq}) \longrightarrow H_2(1\ atm) && \Delta F = -RT \ln P_{H_2}(eq)
\end{aligned}$$

$$Ca(\beta\text{-soln}) + H_2(P\ eq) \rightleftharpoons CaH_2(soln) \qquad \Delta F = 0$$

By summing the above equations for ΔF one obtains:

$$\Delta F^{o}_{CaH_2} = \overline{\Delta F}_{Ca} - \overline{\Delta F}_{CaH_2} + RT \ln P_{H_2}(eq)$$

or

$$\Delta F^{o}_{CaH_2} = RT \ln a_{Ca} - RT \ln a_{CaH_2} + RT \ln P_{H_2\ eq} . \qquad (3)$$

As is indicated by this Equation it is necessary to know the equilibrium activity of calcium and the activity of calcium hydride as well as the experimentally determined

equilibrium hydrogen pressures to obtain the thermodynamic properties of CaH_2. The equilibrium activities may be estimated from the phase diagram.

The solubility of hydrogen in calcium for the experimental temperature range of this investigation has been determined by Peterson and Fattore (9). (See Table 5).

Table 5. Solubility of hydrogen in calcium for the temperature range 600-780°C according to Peterson and Fattore (9)

Temperature °C	N_{Ca}	N_{H_2}
615	.93	.07
650	.92	.08
655	.91	.09
715	.89	.11
733	.87	.13
760	.86	.14
775	.83	.17

According to Sievert's law diatomic gases dissolve atomically in metals. In the case of the dissolution of hydrogen in calcium, Treadwell and Stechers' (3) data indicate that this is true. This being the case it is possible to relate the equilibrium hydrogen pressure; mole fraction of hydrogen, N_H; and the activity of hydrogen as follows:

$$a_{H_2} = P_{H_2} = kN_H^2 .$$

Then according to the Gibbs-Duhem equation

$$N_{Ca}\ d\ \ln\ a_{Ca} = N_{H_2}\ d\ \ln\ a_{H_2} = -N_{H_2}\ d\ \ln\ kN_H^2 .$$

At a given temperature k remains constant and N_H in terms of the variables N_{Ca} and N_{H_2} is given by the relation

$$N_H = \frac{2N_{H_2}}{N_{H_2}+1} .$$

The Gibbs Duhem equation can therefore be written as

$$d\ \ln\ a_{Ca} = \frac{-2N_{H_2}}{1-N_{H_2}}\ d\ \ln\ \frac{2N_{H_2}}{N_{H_2}+1} .$$

Upon substituting $N_{H_2} = 1-N_{Ca}$ into the above expression one obtains

$$d\ \ln\ a_{Ca} = \frac{2(N_{Ca}-1)}{N_{Ca}}\ d\ \ln\ \frac{2(1-N_{Ca})}{(2-N_{Ca})} .$$

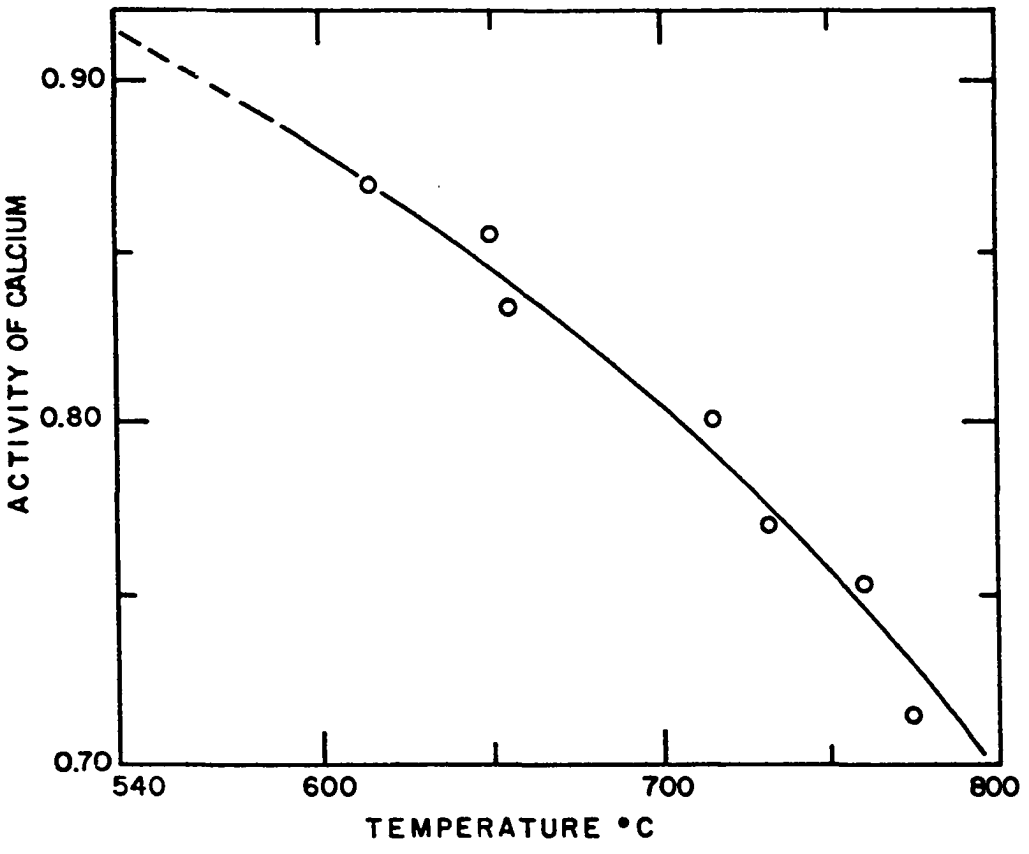
Integration of this relation with the condition that $a_{Ca} \longrightarrow 1$ as $N_{Ca} \longrightarrow 1$ yields the relation

$$a_{Ca} = \frac{N_{Ca}}{2-N_{Ca}} . \qquad (4)$$

Utilizing the data given in Table 5, the activity of calcium can be calculated. A plot of a_{Ca} vs T^oC is given in Figure 7.

The calcium-calcium hydride phase diagram shown in Figure 6 as well as the data of Treadwell and Stecher (3) indicate that the average composition of the CaH_2 rich solid solution is approximately 95 mole per cent in the temperature range 200-780°C. For the purpose of this calculation, the

Figure 7. Activity of calcium in the calcium-rich solution as a function of temperature


0.90
0.80
0.70
ACTIVITY OF CALCIUM
540
600
700
800
TEMPERATURE °C

activity of calcium hydride in the calcium hydride-rich solution was assumed to be 0.95.

Equation 3 may be written as

$$\Delta F^{o}_{CaH_2} = -RT \ln \frac{a_{CaH_2}}{a_{Ca}P_{H_2}} = -RT \ln K. \qquad (5)$$

The activity of calcium obtained from Figure 7, the measured equilibrium hydrogen pressure and the activity of calcium hydride as estimated from the mole fraction were combined in order to calculate log K for each experimentally determined pressure. The results of this calculation are given in Table 6. A plot of log K vs $10^4/T$ is given in Figure 8 for the temperature range 578-780°C. A least squares treatment of the data yields

$$\log K = \frac{9241}{T} - 6.890. \qquad (6)$$

Substituting this relation in Equation 5 gives

$$\Delta F^{o}_{CaH_2} = -42,278 + 31.52T \quad (440\text{-}780^{o}C) \qquad (7)$$

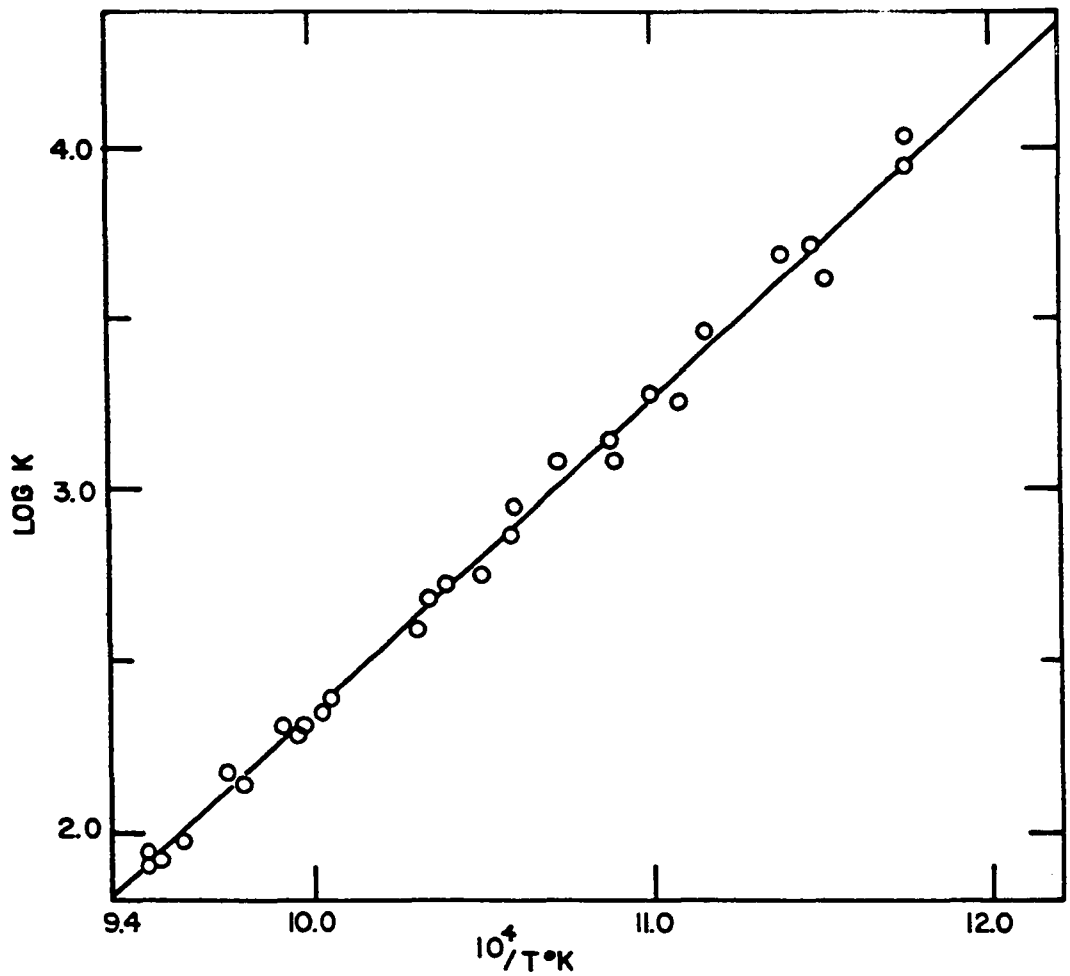
for the reaction $Ca(\beta) + H_2$ (1 atm) $\longrightarrow CaH_2(\alpha)$. The probable errors in the two constants as calculated from the least squares treatment of the data in Table 6 are 440 and 0.46 respectively. It was not possible to take ΔCp for the reaction into account due to lack of heat capacity data for calcium hydride. The difference in heat capacities in the temperature range of the measurements is probably very small.

It is necessary to consider the free energy change for

Table 6. Log K calculated from the equilibrium hydrogen pressure, the activity of calcium and the activity of calcium hydride

Temperature ^{o}K	$10^4/T^{o}K$	$\log \frac{a_{CaH_2}}{a_{Ca}P_{H_2}}$
851	11.75	3.967
851	11.75	4.059
869	11.51	3.631
872	11.47	3.732
878	11.39	3.701
896	11.16	3.471
903	10.07	3.256
910	10.98	3.281
919	10.88	3.088
920	10.87	3.145
933	10.72	3.088
944	10.59	2.951
945	10.58	2.858
953	10.49	2.741
963	10.39	2.716
967	10.34	2.683
970	10.30	2.592
995	10.05	2.383
998	10.02	2.345
1003	9.97	2.301
1004	9.96	2.289
1009	9.91	2.298
1021	9.79	2.131
1026	9.75	2.172
1029	9.72	2.105
1041	9.61	1.979
1047	9.55	1.917
1051	9.51	1.950
1052	9.51	1.927

Figure 8. Common logarithm of the equilibrium constant for the reaction $Ca(\beta) + H_2(P_{eq}) \longrightarrow CaH_2(\alpha)$ as a function of $10^4/T^oK$


4.0
3.0
2.0
LOG K
9.4
10.0
11.0
12.0
$10^4/T°K$

the transformation $Ca(\alpha) \longrightarrow Ca(\beta)$ in order to obtain room temperature values for the thermodynamic properties of CaH_2. According to K. K. Kelley (19) the heat capacity for the two allotropic forms of calcium and the enthalpy of transition are given by the relations

$$C_p(\alpha) = 5.25 + 3.44 \times 10^{-3}T,$$

$$C_p(\beta) = 2.68 + 6.80 \times 10^{-3}T,$$

and

$$\Delta H_{trans.} = 270.$$

Due to the lack of heat capacity data for calcium hydride it was felt that the use of a temperature dependent expression for $\Delta C_p(Ca(\alpha) \longrightarrow Ca(\beta))$ was not warranted.

The average value of ΔC_p for the temperature range 298-713°K was calculated to be -0.84 cal/deg. This average value of ΔC_p was combined with the enthalpy of transformation to give

$$\Delta F^o = 868 - 6.74T + 1.93T \log T \qquad (8)$$

for the transformation

$$Ca(\alpha) \longrightarrow Ca(\beta). \qquad (9)$$

Adding Equation 8 to Equation 7 yields

$$\Delta F^o_{CaH_2}(\alpha) = -41{,}410 + 24.78T + 1.93T \log T \ (25\text{-}440^oC) \qquad (10)$$

for the reaction

$$Ca(\alpha) + H_2(1 \text{ atm}) \longrightarrow CaH_2(\alpha).$$

Values for the standard free energy, enthalpy, and entropy

of formation of CaH_2 at various temperatures are given in Table 7.

Table 7. Free energy, enthalpy, and entropy of formation of CaH_2

Temp. °C	$-\Delta F^\circ$ cal/mole	$-\Delta H^\circ$ cal/mole	$-\Delta S^\circ$ cal/mole-deg.
25	32,610	41,650	30.4
400	21.060	41,980	31.1
500	17,910	42,280	31.5
600	14,760	42,280	31.5
700	11,610	42,280	31.5

The equilibrium hydrogen pressures for the temperature range 780-890°C were employed in the calculation of the standard free energy of formation of β-CaH_2. The method used was similar to that employed for the calculation of the free energy of formation of α-CaH_2. The calcium-calcium hydride phase diagram shown in Figure 6 indicates that neither the composition of the calcium-rich solution nor the composition of the calcium hydride-rich solution varies greatly in the temperature range 780-890°C. The average composition of the calcium rich solution was taken to be 22 mole % CaH_2 while that of the calcium hydride-rich phase was taken to be 95 mole % CaH_2. The activity of

calcium, estimated by the method described previously, was calculated to be 0.695 for the temperature range 780 to 890°C. The activity of CaH_2 was assumed to be equal to the mole fraction, 0.95. These activities were combined with the equilibrium hydrogen pressure to obtain

$$\Delta F^{\circ}_{CaH_2(\beta)} = -4.574T \log \frac{a_{CaH_2(\beta)}}{a_{Ca(\beta)} P_{H_2}} = -4.575T \log \frac{0.95}{0.695} - \log P_{H_2} \quad . \quad (11)$$

The measured equilibrium hydrogen pressure for the temperature range 780 to 890°C, Equation 2, is given by the relation

$$\log P_{H_2}(atm) = \frac{-8890}{T} + 6.66. \quad (12)$$

Substituting this relation in Equation 11 and assuming ΔC_p is negligible, yields

$$\Delta F^{\circ}_{CaH_2(\beta)} = -40,672 + 29.85T \quad (13)$$

for the reaction

$$Ca(\beta) + H_2 \longrightarrow CaH_2(\beta).$$

The expression for the standard free energy of formation of α-CaH_2 given by Equation 7 was subtracted from Equation 13 to give

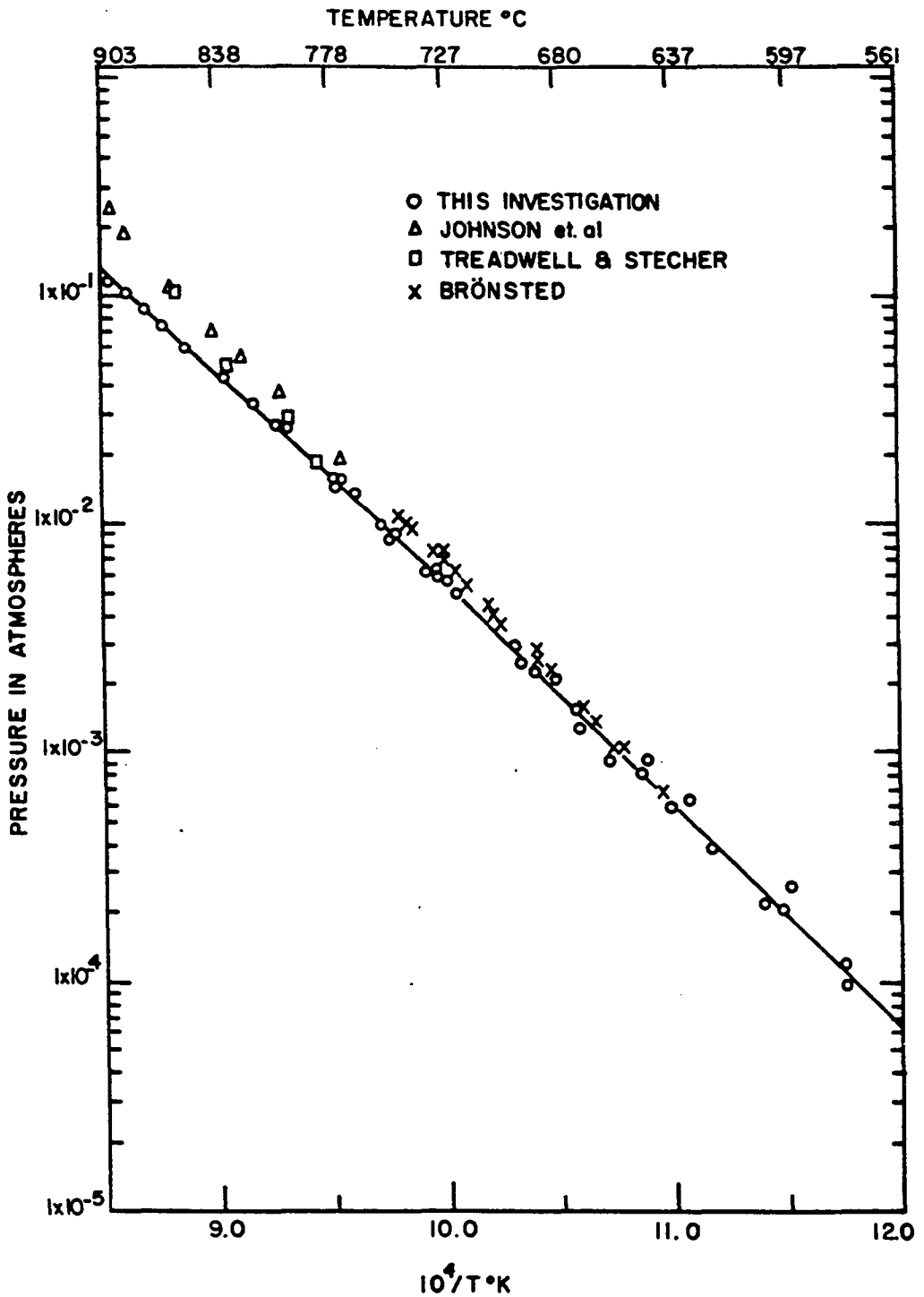
$$\Delta F^{\circ} = 1606 - 1.67T$$

for the transformation $CaH_2(\alpha) \longrightarrow CaH_2(\beta)$.

Discussion of Results

The value of 30.4 obtained for the standard entropy of formation of CaH_2 at 298°K agrees well with the value predicted by Lewis and Randall (6). It is very unlikely that this entropy value can be in error by more than ± 0.5 entropy units. The uncertainty in the entropy determined from Equation 7 for the temperature range 578-780°C is calculated from a least squares treatment of the data to be ± 0.46 entropy units. The probable error in the enthalpy for the same temperature range is similarly calculated to be ± 0.44 kilo calories. The thermodynamic values were calculated on the basis of the data taken in the temperature range 578-780°C, however, pressure measurements were also made in the temperature range 780-900°C. These data along with data obtained by other investigators are shown in Figure 9. The pressures in the higher temperature range were found to be lower than those reported by Treadwell and Stecher (3) and Johnson et al. (4). Since calcium metal is often contaminated with magnesium, this discrepancy may be due to magnesium in the calcium used in their investigations. Johnson et al. (4) report that their starting material was 97.12% calcium as determined by an oxylate precipitation. After a double distillation the analysis of their metal was 99.5% calcium. The method of analysis may not, however,

Figure 9. Comparison of data obtained in this investigation with that given in the literature


TEMPERATURE °C
903
838
778
727
680
637
597
561
O THIS INVESTIGATION
Δ JOHNSON et. al
□ TREADWELL & STECHER
x BRÖNSTED
PRESSURE IN ATMOSPHERES
1x10-1
1x10-2
1x10-3
1x10-4
1x10-5
9.0
10.0
11.0
12.0
10⁴/T °K

give a true indication of the amount of magnesium present since magnesium may have been coprecipitated with the calcium. Treadwell and Stecher (3) give no specific analysis of the calcium employed but do state that the calcium was doubly distilled. Brönsted (5) measured the dissociation pressure of calcium hydride in the temperature range 641-745°C. The pressures obtained by Brönsted agree quite well with those obtained in this investigation. However, the slope of the line obtained from a plot of log P_{H_2}(atm) vs $10^4/T^\circ K$ from Brönsted's data is appreciably different from that obtained in this investigation. The fact that the metal used in his investigation only analyzed 97.3% calcium could have caused this deviation.

III. THERMODYNAMIC PROPERTIES OF $CaMg_2$

Materials and Experimental Procedure

The calcium employed in the preparation of the alloys used in this investigation was the same as that described in the preceding section. A chemical analysis of the magnesium employed is given in Table 8.

Table 8. Chemical analysis of magnesium

Element	Content in ppm
C	250
N	45
O	30
Fe	40
Si	Trace
Ca	Trace

A magnesium-38 wt % calcium alloy was prepared by heating the constituents in a sealed tantalum crucible under a helium atmosphere. To insure adequate mixing and to obtain a homogeneous alloy, the metals were heated to 850°C and agitated in a rotating furnace for 2 hours. The alloy was water quenched to room temperature.

The apparatus and experimental procedure employed in the investigation of the equilibrium hydrogen pressures

over a magnesium-38 wt % calcium alloy was similar to that described in the preceding section for the investigation of the dissociation pressure of calcium hydride. An iron crucible was outgassed, a sample of magnesium-38 wt % calcium weighing approximately 3 grams was placed in the crucible, the crucible was sealed with a thin iron foil under a hydrogen atmosphere, the crucible and its contents were placed in the reaction tube shown in Figure 3 and enough hydrogen was admitted to the system to convert about 50% of the calcium to CaH_2. The sample was heated to 550°C to enable the calcium to react with the hydrogen. After a constant hydrogen pressure was attained, the system was evacuated and held at the same temperature until the pressure remained constant for a period of 12 hours. The pressure returned to the same equilibrium value in all cases. The system was assumed to be at equilibrium when the pressure remained constant for a period of 8-12 hours. The time for reaching equilibrium varied from 9 days at 462°C to 2 days at 608°C. The relatively long periods of time required to attain equilibrium at the low temperatures prompted the investigation of other materials to replace iron foil as a semi-permeable membrane. Copper, platinum and tantalum were tried but all three proved unsatisfactory. The copper and platinum appeared to react with the alloy while the tantalum became extremely brittle in the hydrogen

atmosphere and cracked almost immediately. Therefore, an iron foil diaphram was used to prevent vaporization of the alloy in all the equilibrium hydrogen pressure measurements.

Experimental Results

The equilibrium hydrogen pressure over a magnesium-38 wt % calcium alloy was measured as a function of temperature. The data obtained are given in Table 9. These data are plotted as log P_{H_2}(atm) vs $10^4/T^\circ K$ in Figure 10. The apparent change in slope at 517°C is due to the eutectic horizontal at this temperature as shown in the calcium magnesium phase diagram according to Hansen and Anderko (15), (See Figure 11). A least squares treatment of the data for the temperature range 450-517°C yields

$$\log P_{H_2}(atm) = \frac{-6919}{T} + 5.954. \qquad (15)$$

The standard deviations in the slope and intercept are 672 and 0.888 respectively. The data for the temperature range 517-608°C were fitted to the best straight line which intersected the line represented by Equation 15 at 517°C. The results of this fit can be expressed as

$$\log P_{H_2}(atm) = \frac{-6666}{T} + 5.63. \qquad (16)$$

A thermodynamic treatment of the data required the knowledge of the phases present at equilibrium. Therefore at the completion of a run a sample of the hydrogenated

Table 9. Equilibrium hydrogen pressures measured over the system consisting of CaH_2, $CaMg_2$, and a magnesium-rich calcium-magnesium solution

Hydrogen pressure in atmospheres x 10^3	Temperature ^oK	$10^4/T^oK$
.1952	725	13.79
.3528	727	13.75
.3668	735	13.60
.4849	752	13.30
.8860	759	13.18
.7718	766	13.05
.8021	766	13.05
1.090	777	12.87
1.341	784	12.76
1.490	787.5	12.70
1.972	797	12.55
2.234	804	12.44
2.669	811	12.33
3.345	821	12.18
3.604	823	12.15
4.138	833	12.00
5.535	846.5	11.81
7.498	863	11.58
10.57	879	11.37
11.03	881	11.35
15.49	894	11.18
20.88	909	11.00

Figure 10. Equilibrium hydrogen pressure measured over magnesium-38 wt % calcium alloy as a function of temperature

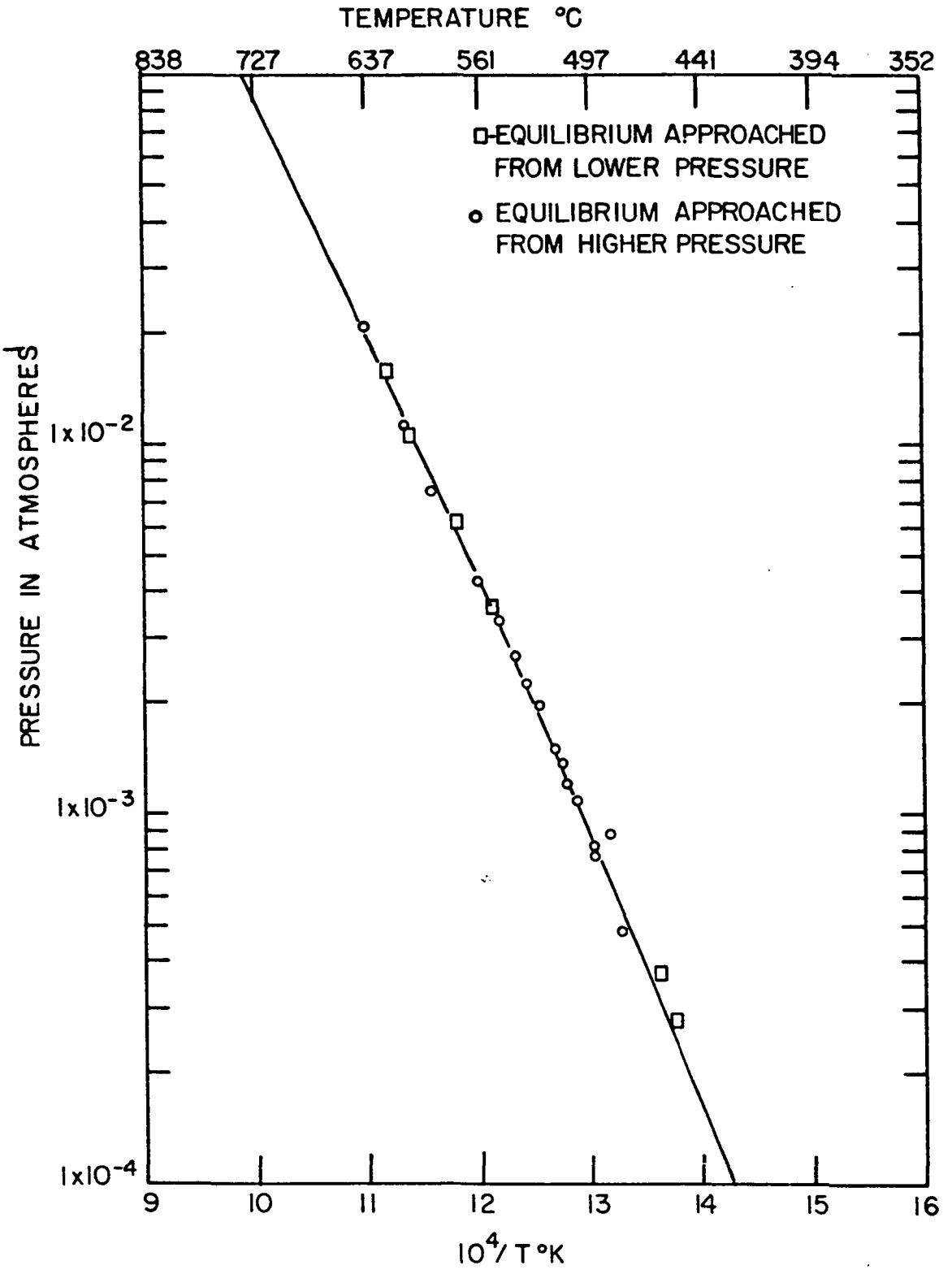
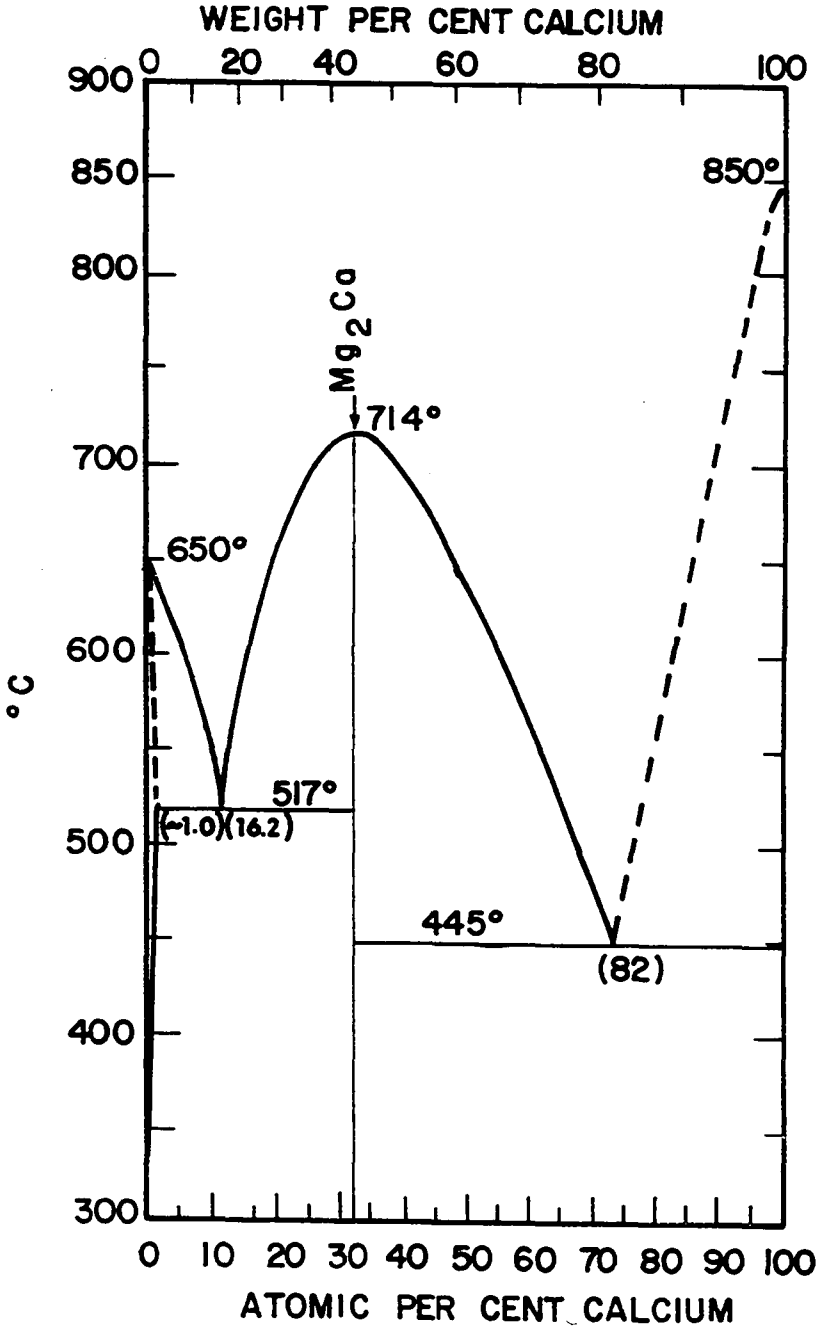

TEMPERATURE °C
838
727
637
561
497
441
394
352
□-EQUILIBRIUM APPROACHED FROM LOWER PRESSURE
o EQUILIBRIUM APPROACHED FROM HIGHER PRESSURE
PRESSURE IN ATMOSPHERES
1x10-2
1x10-3
1x10-4
9
10
11
12
13
14
15
16
10⁴/T °K

Figure 11. Calcium-magnesium phase diagram (After Hansen and Anderko)


WEIGHT PER CENT CALCIUM
0
20
40
60
80
100
900
850
800
700
600
500
400
300
°C
850°
Mg_2Ca
714°
650°
517°
(~1.0)
(16.2)
445°
(82)
0
10
20
30
40
50
60
70
80
90
100
ATOMIC PER CENT CALCIUM

alloy was prepared for x-ray analysis in the same manner as was described in the preceding section for calcium-calcium hydride. An x-ray diffraction pattern was taken with a Debye-Scherrer powder camera. The resulting "d" spacings and relative intensities are tabulated in Table 10 along with literature values (18) for the "d" spacings and relative intensities of CaH_2, $CaMg_2$ and magnesium. The first 37 lines, with the exception of 1 very weak line, could be indexed on the basis of CaH_2, $CaMg_2$ or magnesium. The extra lines, all of which were very weak, could be due to minor amounts of impurities. Calcium hydride is very reactive toward atmospheric moisture and small amounts of moisture adsorbed on the porcelain mortar could have reacted with the calcium hydride to form such compounds as calcium hydroxide or calcium oxide. Even though the weak lines cannot all be accounted for on the basis of the reported "d" spacings for CaH_2, $CaMg_2$ and magnesium the strong lines show that the sample was composed primarily of these three phases.

Thermodynamic Analysis

The method used in the determination of the thermodynamic properties of $CaMg_2$ is best illustrated by considering the following reactions:

Table 10. Comparison of the observed "d" spacings and relative intensities obtained from the hydrided magnesium-38 wt % calcium with those given in the A.S.T.M. files for CaH_2, $CaMg_2$ and magnesium

d-Obs	Obs. R.I.	"d"-CaH_2	(CaH_2) Rel.Int.	"d"-$CaMg_2$	($CaMg_2$) Rel.Int.	"d"-Mg	(Mg) Rel.Int.
3.42	VVW						
3.19	VS	3.18	40				
3.12	W			3.14	44		
2.98	VVS	2.97	100				
2.87	S			2.87	75		
2.81	VVS	2.81	80			2.78	35
2.65	VS			2.65	100		
2.61	S	2.63	8			2.60	41
2.45	VS					2.45	100
2.41	W	2.40	8	2.40	8		
2.18	VS	2.17	40				
1.93	VS	1.92	28				
1.90	VVW			1.90	5	1.90	20
1.83	W	1.82	8				
1.80	W	1.79	20	1.80	5		
1.75	W			1.75	31		
1.72	W	1.71	24				
1.70	VW			1.70	25		
1.69	S	1.68	24				
1.62	S	1.61	20	1.62	20	1.60	18
1.56	VW			1.56	15		
1.54	S	1.54	36				
1.49	VVW						
1.48	W	1.48	8			1.47	8
1.38	VVW	1.38	4			1.38	2
1.37	W			1.37	8	1.37	10
1.35	W	1.35	4	1.34	5	1.34	3

Table 10. (Continued)

d-Obs.	Obs. R.I.	"d"-CaH_2	(CaH_2) Rel.Int.	"d"-$CaMg_2$	($CaMg_2$) Rel.Int.	"d"-Mg	(Mg) Rel.Int.
1.25	W	1.25	36				
1.25	VW						
1.24	VW			1.23	3	1.23	2
1.18	VW	1.18	8			1.18	2
1.16	VVW			1.17	3		
1.16	VVW						
1.15	VVW	1.15	8	1.15	3		
1.14	VVW			1.13	3		
1.12	VVW	1.12	4				
1.11	VVW						
1.10	VVW						
1.08	VVW					1.09	2
1.07	VVW	1.07	4				
1.06	VVW					1.06	1
1.02	VVW	1.02	4			1.03	7
1.00	VVW					1.01	3
1.00	VVW						
.955	VVW						
.953	VVW						
.950	VVW					.951	1
.898	VVW					.899	4
.896	VVW						
.892	VVW						
.890	VVW						
.871	VVW					.873	2
.866	VVW						
.862	VVW						
.860	VVW						
.840	VVW						

Table 10. (Continued)

d-Obs.	Obs. R.I.	"d"-CaH_2	(CaH_2) Rel.Int.	"d"-$CaMg_2$	($CaMg_2$) Rel.Int.	"d"-Mg	(Mg) Rel.Int.
.823	VVW						
.821	VVW						
						.818	1
.721	VVW						
.798	VVW						
.796	VVW						
.775	VVW						

$$CaMg_2(s) + H_2(1\ atm) \longrightarrow CaH_2(s) + 2Mg(s) \qquad \Delta F = \Delta F^{o}_{CaH_2} - \Delta F^{o}_{CaMg_2}$$

$$H_2\ (P\ eq) \longrightarrow H_2(1\ atm) \qquad \Delta F = -RT \ln P_{H_2}(eq)$$

$$2Mg\ (s) \longrightarrow 2Mg(s\text{-soln}) \qquad \Delta F = 2\ \overline{\Delta F}_{Mg}$$

$$CaMg_2(s) + H_2(P\ eq) \rightleftharpoons CaH_2 + 2Mg(s\text{-soln}) \qquad \Delta F = 0$$

The symbols (s), (S-soln) and $P_{H_2}eq$ represent the solid state, solid solution and equilibrium hydrogen pressure respectively. Summing the above equations for ΔF yields

$$\Delta F^{o}_{CaMg_2} = \Delta F^{o}_{CaH_2} - RT \ln P_{H_2}(eq) + 2\ \overline{\Delta F}_{Mg}. \qquad (17)$$

The solubility of calcium in magnesium is very low for the temperature range 365-518°C as reported by Burke (16), (see Table 1). Therefore, it can be assumed that $\overline{\Delta F}_{Mg} = 0$ for this temperature range and Equation 17 reduces to

$$\Delta F^{o}_{CaMg_2} = \Delta F^{o}_{CaH_2} - RT \ln P_{H_2}(eq). \qquad (18)$$

Substitution of the expression for the free energy of formation of CaH_2 given by Equation 7 and the expression for log P_{H_2} given by Equation 15 into Equation 18 gives the relation

$$\Delta F^{o}_{CaMg_2} = -10,624 + 4.24T \quad (440\text{-}517^{o}C). \qquad (19)$$

Due to lack of heat capacity data for $CaMg_2$ no correction can be made for the ΔC_p of the reaction $Ca(\beta\text{-}\delta) + 2Mg(s) \longrightarrow CaMg_2(s)$. The expression for the free energy of transformation of calcium, Equation 8, may be combined with Equation 19 to give

$$\Delta F^{o}_{CaMg_2} = -9,735 - 2.46T + 1.93T \log T \quad (25\text{-}440^{o}C) \qquad (20)$$

for the reaction

$$Ca(\alpha) + 2Mg(s) \longrightarrow CaMg_2.$$

The thermodynamic expressions $\frac{d(\frac{\Delta F^o}{T})}{d\ \frac{1}{T}} = \Delta H^o$ and $\frac{d\,\Delta F^o}{dT} = -\Delta S^o$ were utilized to obtain the following expression for the standard enthalpy and entropy of formation of $CaMg_2$:

$$\Delta H^o_{CaMg_2} = -10,624 \qquad (440\text{-}517^oC),$$

$$\Delta S^o_{CaMg_2} = -4.28 \qquad (440\text{-}517^oC),$$

$$\Delta H^o_{CaMg_2} = -9,735 - 0.84T \qquad (250440^oC),$$

and

$$\Delta S^o_{CaMg_2} = 1.62 - 1.93 \log T \qquad (25\text{-}440^oC).$$

Values for the free energy, the enthalpy and the entropy of formation of $CaMg_2$ at various temperatures are tabulated in Table 11.

Table 11. Free energy, enthalpy and entropy of formation of $CaMg_2$ at various temperatures.

Temp. °C	$-\Delta F^o$(cal/mole)	$-\Delta H^o$(cal/mole)	$-\Delta S^o$(cal/mole deg)
25	9,045	9,985	3.16
300	8,090	10,216	2.70
400	7,717	10,300	3.84
450	7,530	10,624	4.28
500	7,316	10,624	4.28

In the temperature range 517-608°C the equilibrium phases were CaH_2, $CaMg_2$ and a magnesium-rich calcium-magnesium liquid solution rather than a solid solution. The free energy of solution of magnesium in this liquid can be obtained from a comparison of the pressure data above and below the eutectic temperature. Let range I be the temperature range 440-517°C and range II be the temperature range 517-608°C. The expressions for $\Delta F^{o}_{CaMg_2}$ for these two temperature ranges, I and II, may be written as

$$\Delta F^{o}_{CaMg_2} = \Delta F^{o}_{CaH_2} - RT \ln P^{I}_{eq}$$

and

$$\Delta F^{o}_{CaMg_2} = \Delta F^{o}_{CaH_2} - RT \ln P^{II}_{eq} + 2\overline{\Delta F}_{Mg(\ell\text{-soln})},$$

respectively. Since the first two terms in each equation are equal

$$2\overline{\Delta F}_{Mg(\ell\text{-soln})} = RT \ln P^{II}_{eq} - RT \ln P^{I}_{eq}.$$

Therefore, substitution of Equation 15 and 16 into the above expression yields

$$\overline{\Delta F}_{Mg\ (\ell\text{-soln})} = 579 - 0.73T \qquad (21)$$

where $\overline{\Delta F}_{Mg}$ represents the free energy change when one mole of magnesium is dissolved in an infinitely large quantity of the calcium-magnesium solution represented by the liquidus line between 16.2 and 40 wt % calcium shown in Figure 11.

Discussion of Results

A comparison of the room temperature values for the thermodynamic properties of $CaMg_2$ obtained by various investigators is given in Table 12. The results of this investigation agree very well with those obtained by Smith and Smythe (10). The enthalpy value is also in good agreement with that obtained by combustion calorimetry as reported by Smith (11). There is also fair agreement between the enthalpy value calculated from lattice parameters by the method of Kubaschewski (12) and that obtained in this investigation. The enthalpy values reported by Kubaschewski and Evans (14) and Rossini et al. (13), which were based on Biltz and Hohorst's (20) solution calorimetry data, are much higher than those obtained in this investigation and those reported by Smith (11). However, as Kubaschewski and Evans (14) point out, data obtained from solution calorimeter measurements are not always reliable, especially for the more reactive metals such as calcium and magnesium. Woerner (1) determined the thermodynamic properties of $CaMg_2$ in a manner similar to that used in this investigation. However, he used an MgO-5% MgF_2 crucible inside the iron crucible to contain the sample. The use of this inner crucible was thought to have caused erroneous results. An experiment was set up wherein an MgO-MgF_2 crucible was used to contain the sample in a manner similar to that employed by Woerner. The

equilibrium hydrogen pressures obtained in this manner were in good agreement with those obtained by Woerner. An x-ray powder pattern taken of the sample at the completion of the run could not be indexed on the basis of $CaMg_2$ and magnesium. However, most of the prominent calcium hydride lines were present. In view of the results of the experiment discussed above, it was concluded that Woerner's results were in error due to the use of an MgO-MgF_2 crucible as a container for the sample.

Table 12. Comparison of various values for the standard free energy, entropy, and enthalpy of formation of $CaMg_2$ at 298°K

Investigators	$-\Delta F^\circ$ cal/mole	$-\Delta H^\circ$ cal/mole	$-\Delta S^\circ$ cal/mole-deg.
This investigation	9,045	9,985	3.16
Smith and Smythe (10)	7,970	8,400	1.20
Woerner (1)	21,220	28,400	24.02
Smith (11)	---	6,900	---
Rossini et al. (13)	---	30,000	---
Kubaschewski and Evans (14)	---	21,300	---
Kubaschewski (12)*	---	13,200	---

*Calculated by Smith (11) from lattice parameters using the method of Kubaschewski.

IV. OTHER COMPOUNDS INVESTIGATED

Several other intermetallic compounds were briefly investigated in an attempt to further check the utility of the reaction of hydrogen with solutes in metals as a method for determining the thermodynamic properties of intermetallic compounds. The compounds investigated were $CaPb_3$, $CaAg_4$, $ThCu_6$, Th_2Ni_{17} and $CaAg_3$. The phase diagrams for the binary systems containing these intermetallic phases are given by Hansen and Anderko (15). The investigation consisted of attempting to react the above intermetallic compounds with hydrogen at temperatures up to 750°C and hydrogen pressures up to one atmosphere. The desired equilibrium for the first four compounds can be represented by

$$A_xB_y(s) + xH_2(g) \rightleftharpoons xAH_2(s) + yB(s),$$

while that for $CaAg_3$ can be represented by

$$4CaAg_3 + H_2 \rightleftharpoons CaH_2 + 3CaAg_4.$$

However, under the experimental conditions given above, none of the compounds appeared to react with hydrogen. This may not be a true indication of the stability of the intermetallic compounds since the kinetic factors entering in the reaction were not considered.

V. SUMMARY

An investigation was made into the applicability of the reaction of hydrogen with solutes in metals as a method for determining thermodynamic properties of intermetallic compounds. The thermodynamic properties of the pure metallic hydride existing at equilibrium must be accurately known in a method of this type. The thermodynamic properties of CaH_2 were obtained by measuring the equilibrium hydrogen pressure over the system consisting of calcium and calcium hydride. The experimentally determined hydrogen pressures were combined with known data for calcium along with known data on the calcium hydrogen system to give the following thermodynamic relations:

$$\Delta F^{o}_{CaH_2} = -42,278 + 31.10T \quad (440\text{-}780^{o}C)$$

and

$$\Delta F^{o}_{CaH_2} = -41,410 + 24.78\ T + 1.93T \log T \quad (25\text{-}440^{o}C).$$

The enthalpy change for the reaction $CaH_2(\alpha) \longrightarrow CaH_2(\beta)$ was calculated to be 1600 cal/mole.

The equilibrium hydrogen pressures over the system consisting of $CaMg_2$, calcium hydride and a magnesium-rich calcium-magnesium solution were measured as a function of temperature. These data were combined with the results of the investigation of the thermodynamic properties of CaH_2 to give the following thermodynamic relations:

$$\Delta F^{o}_{CaMg_2} = -10,624 + 4.28T \quad (440\text{-}517^{o}C)$$

and

$$\Delta F^{o}_{CaMg_2} = -9{,}735 - 2.46T + 1.93T \log T \quad (25\text{-}440^{o}C).$$

An attempt was made to react $CaPb_3$, $CaAg_4$, $CaAg_3$, $ThCu_6$, and Th_2Ni_{17} with hydrogen at pressures up to one atmosphere and temperatures up to 700°C, however, none of the compounds were found to react with hydrogen when subjected to this treatment.

It appears that the applicability of the reaction of hydrogen with solutes in metals as a method for determining the thermodynamic properties of intermetallic compounds is very limited. Some of the factors which seem to limit this method are: the compound or alloy must react with hydrogen to form a stable hydride in the temperature range of interest, the equilibrium hydrogen pressures must be of such magnitude that they are measurable, one must be able to identify the phases present at equilibrium, and the thermodynamic properties of the pure metallic hydride phase present at equilibrium must be accurately known. The determination of the thermodynamic properties of metal hydrides is complicated by the fact that many of the metal-metal hydride systems are very complex.

VI. LITERATURE CITED

1. Woerner, P. F. Separation of metals as hydrides from liquid metal solutions. Unpublished Ph.D. Thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. (1960).

2. University of Denver. Denver Research Institute. Investigation of hydriding characteristics of intermetallic compounds. U. S. Atomic Energy Commission Report LAR-53 Lockland Aircraft Reactors Operations Office, AEC (1961).

3. Treadwell, W. D. and Stecher, J. Über den Wasserstoffdruck von calciumhydrid. Helvetica Chemica Acta 36: 1820 (1953).

4. Johnson, W. D., Stubbs, M. F., Sidwell, A. E. and Peahukas, A. The rate of formation and the dissociation of calcium hydride. American Chemical Society Journal 61: 318 (1939).

5. Brönsted, J. N. Zur thermodynamik der calciumwasserstoffdruckbildung. Zeitschrift für Electrochemie. 20: 81 (1914).

6. Lewis, G. N. and Randall, M. Thermodynamics. New York, N.Y., McGraw-Hill Book Co., Inc. (1923).

7. Smith, J. F. and Bernstein, B. T. Effects of impurities on crystallographic modifications of calcium metal. Electrochemical Society Journal 106: 448 (1959).

8. Smith, J. F., Carlson, O. N. and Vest, R. W. Allotropic modifications of calcium. Electrochemical Society Journal 103: 409 (1956).

9. Peterson, D. T. and Fattore, V. G. Calcium-calcium hydride phase system. Journal of Physical Chemistry 65: 2062 (1961).

10. Smith, J. F. and Smythe, R. L. Vapor pressure measurements over calcium, magnesium, and their alloys and the thermodynamics of formation of $CaMg_2$. Acta Metallurgica 7: 261 (1950).

11. Smith, J. F. Determination of thermodynamic functions for the formation of binary intermetallic phases from vapor pressure measurements. U. S. Atomic Energy Commission Report IS-440 Iowa State University of Science and Technology, Ames. Inst. for Atomic Research (1961).

12. Kubaschewski, O. The physical chemistry of metallic solutions and intermetallic compounds. Volume 1. London, England, Her Majesty's Stationary Office. (1959).

13. Rossini, F., Wagman, D. D., Evans, W. H., Levine, S. and Jaffe, I. Selected values of chemical thermodynamic properties. U. S. Bureau of Standards Circular 500. (1952).

14. Kubaschewski, O. and Evans, E. L. Metallurgical thermochemistry. 3rd ed. New York, N. Y., Pergamon Press. (1958).

15. Hansen, M. and Anderko, K. Constitution of binary alloys. 2nd ed. New York, N. Y., McGraw-Hill Book Co., Inc. (1958).

16. Burke, E. C. Solid solubility of calcium in magnesium. American Institute for Mining, Metallurgical and Petroleum Engineering Transactions 203: 285 (1955).

17. Williamson, A. T. The exact calculation of heats of solution from solubility data. Faraday Society Transactions 40: 412 (1944).

18. American Society for Testing Materials. Index to the x-ray powder data file. Philadelphia, Pa., Author. (1961).

19. Kelley, K. K. Contributions to the data on theoretical metallurgy. U. S. Bureau of Mines Bulletin 584. (1960).

20. Biltz, W. and Hohorst, G. Die bildungswarmen der verbindungen von metallishem magnesium mit metallishem zinc, cadmium, aluminum und calcium. Zeitschrift für anorganische und allgemeine chemie. 121: 1 (1922).

VII. ACKNOWLEDGMENTS

The author wishes to express sincere gratitude to Dr. Premo Chiotti for his invaluable guidance during the course of this investigation and in the preparation of this manuscript.

Thanks is also extended to the other members of Metallurgy Group IV for their helpful advice and constructive criticism.

The author is especially grateful to his wife, Rita, for her patience and encouragement during the course of his graduate work.

VIII. APPENDIX

Derivation of an expression for $\overline{\Delta H}_{CaMg_2}$ in terms of the solid solubility of calcium in magnesium.

Let phase I be the magnesium-rich calcium-magnesium solid solution and phase II be the compound $CaMg_2$. Since the two phases are in equilibrium, the same reference state can be chosen for component i. Therefore, the activity of component i in phase I is equal to the activity of component i in phase II. Let component i be $CaMg_2$. Then

$$a^{I}_{CaMg_2} = a^{II}_{CaMg_2}$$

or

$$N^{I}_{CaMg_2} \gamma^{I}_{CaMg_2} = N^{II}_{CaMg_2} \gamma^{II}_{CaMg_2} .$$

Where the superscripts represent the phases and the subscripts represent the components under consideration. Phase II is solid $CaMg_2$ of essentially constant composition. Therefore, if solid $CaMg_2$ is chosen as the reference state it follows that

$$a^{II}_{CaMg_2} = 1$$

and

$$N^{I}_{CaMg_2} \gamma^{I}_{CaMg_2} = 1,$$

where γ and N represent activity coefficient and mole fraction respectively.

Taking the natural logarithm of both sides of the above equation and differentiating partially with respect to reciprocal temperature yields

$$\left(\frac{\partial \ln N_{CaMg_2}}{\partial 1/T}\right)_P + \left(\frac{\partial \ln \gamma_{CaMg_2}}{\partial 1/T}\right)_P = 0. \qquad (1a)$$

In order to evaluate the second term of Equation 1a consider γ_i as a function of the temperature and composition of component i [i.e. $\gamma_i = \gamma_i(T, N_i)$] , where i still represents $CaMg_2$. Taking the natural logarithm and the total derivative of γ_i with respect to 1/T gives

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_P = \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{N_i}\left(\frac{\partial T}{\partial 1/T}\right)_P + \left(\frac{\partial \ln \gamma_i}{\partial N_i}\right)_T\left(\frac{\partial N_i}{\partial 1/T}\right)_P$$

or

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_P = \left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{N_i} + \left(\frac{\partial \ln \gamma_i}{\partial N_i}\right)_T\left(\frac{\partial N_i}{\partial 1/T}\right)_P.$$

Substitution of the identity $\partial \ln N_i = \frac{\partial N_i}{N_i}$ into the latter term of the above expression yields

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_P = \left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{N_i} + N_i\left(\frac{\partial \ln \gamma_i}{\partial N_i}\right)_T\left(\frac{\partial \ln N_i}{\partial 1/T}\right)_P.$$

It can be shown that (See Lewis and Randall (6) page 279)

$$\left(\frac{\partial \ln a_i}{\partial 1/T}\right)_{N_i} = \frac{\overline{\Delta H_i}}{R} = \left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{N_i}.$$

where $\overline{\Delta H_i}$ represents the partial molar heat of solution of component i. Therefore

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_P = \frac{\overline{\Delta H_i}}{R} + N_i \left(\frac{\partial \ln \gamma_i}{\partial N_i}\right)_T \left(\frac{\partial \ln N_i}{\partial 1/T}\right)_P . \qquad (2a)$$

Substituting Equation 2a into 1a, substituting i = $CaMg_2$ and rearranging gives the relation

$$\left(\frac{\partial \ln N^I_{CaMg_2}}{\partial 1/T}\right)_P \left[1 + N^I_{CaMg_2}\left(\frac{\partial \ln \gamma^I_{CaMg_2}}{\partial N^I_{CaMg_2}}\right)_T\right] = -\frac{\overline{\Delta H}_{CaMg_2}}{R} .$$

In dilute solutions where Henry's law is expected to hold such as the one we are considering one can say

$$\left(\frac{\partial \ln \gamma^I_{CaMg_2}}{\partial N^I_{CaMg_2}}\right)_T = 0 .$$

Therefore

$$\left(\frac{\partial \ln N^I_{CaMg_2}}{\partial 1/T}\right)_P = -\frac{\overline{\Delta H}_{CaMg_2}}{R} .$$